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Krzysztof Matyjaszewski, Karen E. Ruehl

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

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Krzysztof Matyjaszewski, Karen E. Ruehl

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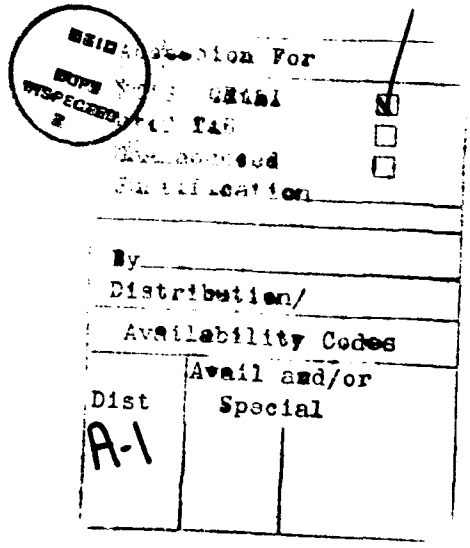

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REDUCTIVE COUPLING OF CHLOROSILANES WITH LITHIUM

Karen E. Ruehl, Krzysztof Matyjaszewski
Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

Abstract:

Reductive coupling of chlorosilanes with lithium in THF proceeds via anionic intermediates (radical anions and silyl anions). They were observed directly by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, EPR and UV spectroscopy.

Introduction:

The electronic, optical, and chemical properties of compounds with Si-Si linkages in the main chain have been studied [1-3]. These properties depend upon chain length, substituents at the Si atoms, chain microstructure, and chain conformation. This strongly resembles other delocalized systems such as polyenes. The most important preparative method leading to Si-Si polymers and oligomers is the reductive coupling of chlorosilanes with alkali metals[1-5]. Reaction of disubstituted dichlorosilanes provides oligo- and polysilanes, whereas reaction of monochlorosilanes should only provide products of direct coupling. Therefore, coupling of 1-chloro-2-phenyltetramethyldisilane should yield 1,4-diphenyloctamethyl-tetrasilane. However, it has been found that in the reaction of 1-chloro-2-phenyltetramethyldisilane with lithium in THF at room temperature, a series of α,ω-diphenyl-permethylated oligosilanes with the formula $Ph(Me_2Si)_nPh$, where n= 2-6, initially forms. In the presence of excess lithium, these oligosilanes are converted to a mixture of cyclic and linear oligosilanes, and eventually into a mixture of monosilyl and disilyl anions, and cyclohexasilane (Scheme 1).

Previously, a thermodynamic distribution of oligosilanes in a similar reaction was studied[6], however, no kinetic aspects were revealed. In this paper, we discuss the mechanism of the coupling and the redistribution processes.

Results

1. Kinetics of the Reaction of 1-Chloro-2-phenyltetramethyldisilane with Lithium

The reaction of 1-chloro-2-phenyltetramethyldisilane with lithium in THF was studied at room temperature using several techniques: HPLC, ^1H NMR, and UV-VIS. Four stages can be distinguished:

I. An induction period depends on the surface property of lithium which is difficult to control. No color change is observed.

II. During the second stage, 1-chloro-2-phenyltetramethyldisilane is converted into a mixture of 1,4-diphenyloctamethyltetrasilane (≈50%), 1,3-diphenylhexamethyltrisilane (≈25%), and 1,5-diphenyldecamethylpentasilane (≈25%). A small amount of 1,2-diphenyltetramethyldisilane and longer oligosilanes can also be detected. The reaction mixture is colorless, however, dark green spots on the surface of lithium can be observed.

III. A strong decrease in the concentration of tetrasilane, as well as penta- and trisilanes is noted during the third stage of the reaction. The disilane becomes the dominating product and dodecamethyl-cyclohexasilane appears. During this stage, green streams which originate at the lithium surface turn red at some distance and decrease in intensity at a further distance, eventually becoming colorless. Soon, the reaction mixture becomes pink, and ultimately deep-red (UV maximum at 450 nm). One of us has described this process as the "bleeding" of lithium. Somewhere during this stage, a nearly thermodynamic product distribution is formed[6] due to the relatively small concentration of anions present in the reaction mixture.

IV. During the fourth stage, the continuous donation of electrons from lithium to the oligosilanes leads to the formation of an equilibrium mixture of phenyldimethylsilyl lithium, 2-phenyltetra-methyldisilyl lithium and dodecamethylcyclohexasilane. The color of the reaction mixture changes from dark red to dark green (maxima at 350, 450 and 650 nm). The NMR shows a mixture of anions and the EPR shows the presence of radicals. If the lithium is removed from the reaction mixture, the color eventually changes back to red and slowly disappears.

2. Characterization of 2-Phenyltetramethyldisilyl Lithium

A variety of monosilyl anions with alkyl and aryl groups have previously been prepared and characterized by spectroscopic methods[7]. The charge in the silyl anions with aryl groups is less delocalized than in analogous carbanions[8]. Disilyl and polysilyl anions have been proposed as intermediates in many reactions but have never been isolated and characterized spectroscopically. One of the reasons is the high reactivity of the Si-Si bonds towards strong nucleophiles and anions which leads to scrambling and redistribution reactions[6]. Polysilyl anions are important intermediates in the synthesis of polysilanes[9].

The disilyl anion was prepared in the reaction of either 1-chloro-2-phenyltetramethyldisilane with lithium, phenyldimethyl-silyl lithium with dodecamethylcyclohexasilane, 1-chloro-3-phenyl-hexamethyltrisilane with lithium, or by reduction of α,ω-diphenyl-oligosilanes with lithium . An equilibrium between the disilyl and monosilyl anions is established in all cases. The disilyl anion is always present simultaneously with the monosilyl anion in approximately a 2:1 ratio in addition to dodecamethylcyclohexasilane.

The products of the reaction have been characterized by ^{1}H NMR,^{13}C NMR, ^{29}Si NMR, and UV-VIS.

The aromatic region in the ^{1}H NMR spectrum of 2-phenyltetramethyldisilyl lithium anion resembles that of phenyldimethylsilyl lithium[8]. A doublet, due to the *ortho* protons, and two triplets, due to the *meta* and *para* protons, are seen for both anions. The downfield shift of the aromatic region for 2-phenyltetramethyldisilyl lithium anion relative to phenyldimethylsilyl anion indicates a decrease in the overall electron density in the ring due to the increased distance between the ring and the anion center. Compared with the monosilyl anion, downfield shifts for *para* (0.29 ppm), *meta* (0.16 ppm) and *ortho* (0.14 ppm) protons in the disilyl anion indicate a weaker delocalization of the negative charge by π-polarization effects[8]. Small signals downfield from the disilyl anions may be ascribed to a small amount of longer oligosilyl anions in which the charge is still less localized onto the aromatic ring. A singlet representing the methyl groups of the monosilyl anion is at 0.052 ppm and two singlets for the disilyl anion are at 0.12 ppm and 0.01 ppm.

The ^{13}C NMR spectra confirm a weaker electron delocalization in disilyl lithium (Table 1) than in the monosilyl lithium (Table 2). A comparison of the ^{13}C NMR chemical shifts for the corresponding chlorides and anions indicates that the *ipso* carbon is shifted downfield by 29 ppm when going from the phenyldimethylsilyl chloride to phenyldimethylsilyl lithium, but only by 11.6 ppm for the disilanes[10]. The *para* carbon atom is shifted upfield by 8.3 ppm for monosilanes, but only 2.9 ppm for disilanes. The chemical shifts of the *ortho* and *meta* carbon signals remain essentially the same for both mono and disilanes.

^{29}Si NMR (DEPT) of the disilyl anion showed two peaks, one at -69.8 ppm (B) which is assigned to the negatively charged silicon atom (42.6 ppm upfield from the monosilyl anion (C)) and the other at -12.6 ppm (A). The coupling constant $J^{1}_{Si\text{-}Si}$ = 31 Hz for the disilyl anion is much less than in phenylpentamethyldisilane (86.1 Hz)[10]. This indicates a weaker coupling between silicon atoms in the anion than in the neutral species. In comparison with the monosilyl anion, the charge in the disilyl anion were located more on the terminal Si atom than on the aromatic group. The spectrum also shows a signal for dodecamethylcyclohexasilane (D) and perhaps longer oligosilyl anions.

A UV study of the mixture of mono and disilyl anions reveal two broad maxima of similar intensities centered at 350 and 450 nm. The first one is ascribed to the well-known monosilyl anion (340 nm)[7]. The second one, which is responsible for the deep red color of the anions solution is ascribed to 2-phenyltetramethyldisilyl lithium. The disilyl anion absorbs at a longer wavelength due to the delocalization of the charge onto the β-phenyl group. Polysilyl anions with an α-phenyl group which are observed in the formation of poly(phenylmethylsilylene) absorb at 390 nm[11]. Thus, the red shift originates in oligosilyl anions which do not contain α-aromatic groups.

3. UV Studies

Due to the large extinction coefficients of the oligosilanes and the parent anions, UV studies were performed for much more diluted solutions than those used in NMR and HPLC studies. Qualitatively, observations similar to those from high concentration experiments were made. The appearance of pink and later a red color corresponds to two maxima, 350 and 450 nm. The first one is the absorption of phenyldimethylsilyl lithium (340 nm)[7], and the second one corresponds to 2-phenyltetramethyldilsilyl lithium. The small red shift of the monosilyl anion may be due to its overlap with the absorption peak of the disilyl anion or due to a second low wavelength maximum of the disilyl anion. Unfortunately, the disilyl anion cannot be prepared alone since it always exists in an equilibrium mixture with the monosilyl anion and dodecamethylcyclohexasilane in a THF solution. The subsequent formation of the green color (650 nm) can be associated with radical anions either based on cyclosilanes, probably decamethylcyclopentasilane, radical anions of α,ω-diphenyloligosilanes, or biphenyl radical anion. The green color observed on the surface of lithium, when no cyclosilanes were present may be ascribed to species formed by electron transfer to oligosilanes with terminal aromatic rings, i.e. the corresponding radical anions.

4. EPR studies

Attempts to detect unpaired electrons in the reaction mixture prior to the formation of the green color were unsuccessful. However, at the final stages of the reaction a strong EPR signal, containing nine lines with intensities 1:4:8:12:14:12:8:4:1 was found. The signal was observed at ambient as well as low temperatures. At 136 K a broader spectrum was found for the

solidified sample. Thermal changes are reversible. In order to associate the coupling to either a polysilane chain or the aromatic rings, a similar reaction with 1-chloro-2-phenyltetramethyldisilane containing a perdeuterated aromatic ring was performed. The reaction behaved in a similar way, but the nine lines collapsed into one signal. This indicates association of the electron with the aromatic ring. EPR spectra resemble those of biphenyl radical anion[14] , but may not be well resolved (no coupling to meta protons observed) due to high spin concentrations, 10^{-3} M. Similiar spectra are expected for radical anions formed from α,ω-diphenyloligosilanes. It is known that the electron is located on the aromatic ring in trimethylsilylbenzene and pentamethyldisilyl-benzene. The electron can also be associated with the aromatic rings of α,ω-diphenylpermethylated olgosilanes. The electron may rapidly exchange its position between rings either via space or via the oligosilane chain leading to line broadening. However, the EPR signal appears at the very end of the reaction when the concentration of α,ω-diphenyloligosilanes is very low. The signal is absent at higher concentrations of oligosilanes. Moreover, it is known that radical anions based on linear oligosilanes decompose easily, for example, the decomposition of diphenyldimethylsilane radical anions is known to form biphenyl radical anions and $[PhSiMe_2PhSiMe_2Ph]^{\cdot -}$ at 20° C[13]. The green color of the reaction mixture could also be assigned to radical anions from decamethylcyclopentasilane[14] . However, the EPR signal is very different from that reported for these species[15]. Thus, we assume that at longer reaction times, some side reactions can lead to silicon-phenyl bond cleavage and formation of a small amount of biphenyl. The concentration of biphenyl is too low to be detected by NMR. This reaction is relatively slow and does not compete with the "normal" coupling, scrambling, and redistribution processes.

5. Model reactions

5.1. Reaction of Dodecamethylcyclohexasilane with Phenyldimethylsilyl Lithium

Phenyldimethylsilyl lithium anion (M^-) reacts rapidly with dodecamethylcyclohexasilane (CHS) to form 2-phenyltetramethyl-disilyl lithium anion (D^-). No longer chain oligosilyl anions were observed in significant amounts. The equilibrium position in this reaction depends on the

concentration of the cyclohexasilane to the 1/6 power (Scheme 2). The estimated value of the equilibrium constant equals K_{eq}= 2.7 $(mol/L)^{1/6}$ in THF at 25 °C. This corresponds to approximately a 2:1 ratio of the disilyl anion to the monosilyl anion at concentrations of dodecamethylcyclohexasilane ≈ 10^{-2} mol/L. The 1/6 exponent indicates that the equilibrium position is not sensitive to the concentration and similiar ratios are expected in the range of 10^{-4} mol/L.

5.2. Reaction of 1-Chloro-3-phenylhexamethyltrisilane with Lithium: An Attempted Synthesis of Trisilyl Anions

The reaction between 1-chloro-3-phenylhexamethyltrisilane and lithium could, in principle, provide 3-phenylhexamethyltrisilyl lithium anions. The coupling reaction was conducted in a manner identical to the coupling of 1-chloro-2-phenyltetramethyldisilane. Again, the reaction yields a mixture of disilyl anion, monosilyl anion and cyclohexasilane. The concentration of the trisilyl anions was too low to be clearly detected by NMR, although small signals downfield from the disilyl anions signal may come from the trisilyl anions. Thus, the trisilyl anions with a γ–aromatic group are less stable than those with α- or β- phenyl groups.

5.3. Reaction of α,ω-Diphenylpermethylated Oligosilanes with Lithium

In a separate reaction 1,4-diphenyloctamethyltetrasilane was reacted in THF with lithium. In this case the reaction started at stage III (Scheme 3). An induction period due to the activation of the surface was observed, but then stages III and IV were identical to the reaction of 1-chloro-2-phenyltetramethyldisilane with lithium. Also, when 1,3- diphenyl-hexamethyltrisilane and 1,5-diphenyl-decamethylpentasilane were reacted with lithium a mixture of cyclohexasilane, monosilyl anion, and disilyl anion was afforded.

5.4. Reaction of Silyl Anions with Silyl Chlorides

A mixture of monosilyl and disilyl anions was reacted with an excess of a variety of monochlorooligosilanes and dichlorooligo-silanes. The silyl anions were introduced into the chlorosilane solution in order to avoid the scrambling process. The reaction of the mixture of anions with 1-chloro-2-phenyltetramethyldisilane provides 1,3-diphenylhexamethyl-trisilane and

1,4-diphenyloctamethyltetrasilane (Eq. 1A). If, however, the chlorosilane was added into a mixture of anions the scrambling process was observed and disilane, pentasilane, and dodecamethylcyclohexasilane were also found (Eq. 1B). Together, these two results indicate that the scrambling process, or Si-Si bond cleavage, is very fast but much slower than the coupling of anions with chlorosilanes. Therefore, no dodecamethyl-cyclohexasilane was formed during stage II.

In the reaction of silyl anions with an excess of either dichlorodimethylsilane, 1,2-dichlorotetramethyldisilane, or 1,3-dichloro-hexamethyltrisilane, a mixture of direacted silanes and unreacted dichlorosilanes was observed (Eq. 2). No monochloro-silanes were found. This was an unexpected result, since Allred and Boberski[3] found predominant formation of monoreacted products using methylmagnesium bromide as a nucleophilic reagent.

Since the formation of direacted product suggests a much higher reactivity of the monochlorosilane than the starting dichlorosilane, competitive reactions of monosilyl anion with a mixture of a) 1,2-dichlorotetramethyldisilane and 1-chloro-2-phenyltetra-methyldilsilane and b) 1,2-dichlorotetramethyldisilane and dichlorodimethylsilane (Eq. 3 a,b) were conducted. If the monophenylated products are indeed much more reactive (Eq. 3a), then the formation of pure 1,3-diphenylhexamethyltrisilane is expected in the presence of an excess of 1,2-dichlorotetramethyl-disilane and 1-chloro-2-phenyltetramethyldisilane (a model of the monoreacted product). In the second case (Eq. 3b), the influence of the chain length on the reactivities of the dichlorosilanes is studied (Eq. 3b). In both cases the reactivities of the chlorosilanes appear to be similar. This result indicates that the silyl anions react with any chlorosilanes in a diffusion controlled process in a THF solution and the reactivities are not structurally dependent. Attempts to estimate relative reactivities by improved mixing were not successful. This observation as well as a colorless solution during stage II indicates an extremely fast coupling reaction of silyl anions with chlorosilanes.

5.5. Coupling of 1-Chloro-2-[p-(dimethylamino)phenyl]tetramethyldisilane with Lithium

The kinetic results indicate that at the very beginning of the reaction, the formation of tetrasilane is accompanied by the formation of trisilane and

pentasilane. This is due to the fact that the electron transfer does not occur directly to the chlorodisilane with the formation of disilyl anions which would eventually couple with another chlorodisilane to form 1,4-diphenyl-octamethyltetrasilane. Instead the electron transfer proceeds to linear oligosilanes which randomly generate mono-, di-, tri-, and etc. silyl anions which eventually produce oligosilanes by coupling with a chlorodisilane.

Thus, it is impossible to selectively prepare the tetrasilane under the typical reaction conditions (THF, 25 °C). Electron donating substituents on the aromatic rings decrease the electron affinity of the oligosilanes and control of the reaction pathway could be obtained. Hence, pure tetrasilane could be prepared (Eq. 4). Indeed, 1-chloro-2-[p-(dimethylamino)phenyl]tetramethyl-disilane reacts with lithium forming exclusively a tetrasilane. Moreover, the surface of the lithium metal during the coupling process remains shiny, in contrast to green spots observed in the reaction of 1-chloro-2-phenyl-tetramethyldisilane. Apparently, oligosilanes with the p-(dimethylamino)-phenyl groups can not efficiently form radical anions. Two electrons are transferred to 1-chloro-2-[p-(dimethyl-amino)phenyl]tetramethyldisilane to form the 2-[p-(dimethylamino)phenyl]tetramethyldisilyl lithium anion which couples with a disilyl chloride to produce the tetrasilane.

Discussion

The overall scheme of the reaction of 1-chloro-2-phenyltetramethyl-disilane with lithium in THF is shown in Scheme 3:

Stage I is the initiation process in which a slow electron transfer from lithium to the disilyl chloride (Cl-2) produces a transient disilyl anion (A-2) which immediately couples with a remaining disilyl chloride to yield linear 1,4-diphenyloctamethyl-tetrasilane (L-4).

Stage II starts when oligosilanes with terminal phenyl groups are present. Relative to the disilyl chloride, the oligomers are much better electron acceptors and the reaction strongly accelerates. Green spots are observed on the lithium surface due to the corresponding radical anions (RA-4). The radical anions either decompose unimolecularly to radicals (R-n) and anions (A-n) or directly attack any remaining disilyl chloride to produce linear oligosilanes and radicals. Also, the radicals may take a second electron from lithium to form anions. They may also recombine, react with solvent, etc. Since no color is observed, the lifetime of the anions appears to be very short

when the disilyl chloride is present. No dodecamethylcyclohexasilane was formed at this stage thus the scrambling reactions are absent. Therefore, at this stage the disilane could be formed by the coupling of two monosilyl radicals or phenyl lithium with the disilyl chloride and not by the scrambling process.

At the end of stage II, "lithium bleeding" is observed. Green streams which eventually turn red are leaving the lithium surface. The streams initially turn colorless very close to the surface, but at longer times remain colored at longer distances. Since the concentration of the disilyl chloride is becoming very low, the lifetime of the anions increases. No scrambling products are found. The rate of the reaction of disilyl chlorides with silyl anions in THF is very fast, probably diffusion controlled. Initially the solution is colorless which indicates the silyl anion concentration to be below 10^{-6} mol/L.

Stage III starts when the disilyl chloride is completely consumed, the linear tetrasilane reaches its maximum concentration and starts to decrease. At the same time the concentration of the linear pentasilane also decreases. The concentration of the disilane increases rapidly and cyclohexasilane appears. At this stage the reaction mixture is deep red and the color intensifies continuously. The UV study reveals two maxima, 350 and 450 nm, corresponding to the monosilyl and disilyl anions. Since the disilyl chloride has been completely consumed, the silyl anions have a longer lifetime. The anions attack Si-Si bonds which leads to the scrambling process. For example, a monosilyl anion may attack an α-Si atom and form a disilane. During the scrambling process, longer and longer oligomers may be formed, of course, with a lower and lower probability. The attack of any silyl anion on the α-Si atom in 1,8-diphenylhexadeca-methyloctasilane produces a heptasilyl anion which may by an end-biting process attack its terminal Si atom and form dodecamethyl-cyclohexasilane and phenyldimethylsilyl lithium (Eq. 5). A similar reaction with an octasilyl anion may generate a disilyl anion and dodecamethylcyclohexasilane. Cyclic compounds are formed only via an extensive scrambling process when longer oligosilyl anions appear. The longer anions are present at very low concentrations. The intermediate anions are continously generated and provide routes to cyclics which are thermodynamic products[15].

Thus, at the end of stage III, the concentration of the anions is still very low, and the relative concentrations of cyclics and linear oligosilanes are determined by their relative stabilities, i.e., by thermodynamics. These concentrations, indicated by the arrow in Figure 1, correspond quite well to those determined previously by Kumada[6]. Kumada studied the equilibration of 1,4-diphenylocta-methyltetrasilane with a catalytic amount of silyl anions. Stage III can be also started from the preformed tetrasilane. In this case, a random cleavage occurs and a thermodynamic distribution is again formed.

At the end of step III, cyclosilanes and oligosilanes of various lengths are present simultaneously with an increasing concentration of silyl anions. Electrons are continously being donated from lithium to oligosilanes to form radical anions which split into anions and radicals. Upon addition of another electron to a radical anion, a dianion is formed which rapidly cleaves into two anions. Thus, longer oligomers are continuously converted to anions. Monosilyl and disilyl anions are more stable than their longer counterparts due to the stabilizing effect of α- or β-phenyl groups. Thus, stage IV is the cleavage of oligosilanes by the continous donation of electrons from lithium leading to the formation of radical anions and anions. A thermodynamic mixture of monosilyl anions, disilyl anions and dodecamethylcyclohexasilane is produced.

The green color at 650 nm and an EPR signal support a structure of a radical anion which is associated with a monosubstituted aromatic ring, probably biphenyl. Thus, similar coupling constant values to those found in literature[16,17] *p*-H atoms (5 G) and to *o*-H atoms (2.8 G) are observed. Coupling to *m*-H atoms is too weak to be detected in the broad lines.

It is difficult to selectively convert disilyl chlorides into tetrasilanes. First, the electron transfer to oligosilanes generates a statistical mixture of trisilane, tetrasilane, and pentasilane. Then, a scrambling process is responsible for the formation of a thermodynamic mixture of a variety of linear and cyclic oligosilanes. Eventually, the continous donation of electrons from lithium generates a mixture of monosilyl anions, disilyl anions and cyclosilanes. Similar problems were reported previously when the coupling of pentamethyldisilyl chloride yielded less than 50% of the expected decamethyltetrasilane[18]. Apparently, electron donating substituents prevent electron transfer and lead to a trong increase in the yield of tetrasilane.

References

1. Miller, R. D. and Michl, J. Chem. Rev., 89, 1989, 1359.

2. West, R. and Maxka, J. Inorganic and Organometallic Polymers; ACS Symposium Series 360; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington DC,1988, Chapter 2.

3. Miller, R. D. Silicon-Based Polymer Science: A Comprehensive Resource; ACS Symposium Series 224; Zeigler, J. M. and Fearon, F. W. G., Eds.; American Chemical Society: Washington DC,1988, Chapter 24.

4. Worsfold, D.J. Inorganic and Organometallic Polymers; ACS Symposium Series 360; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington DC,1988, Chapter 8.

5. Kumada, M. and Tamao, K. Adv. Organomet. Chem, 1968, 6, 19.

6. Kumada, M.; Sakamoto, S.; Ishikawa, M. J. Organomet. Chem., 1969,17, 231.

7. Davis, D. and Gray, C. Organometal. Chem. Rev. A, 1970, 6, 283.

8. Buncel, E.; Venkatachalam, T.K.; Eliasson, B.; Edlund, U. J. Am. Chem. Soc., 1985, 107, 303.

9. Cypryk, M.; Gupta, Y.; Matyaszewski, K. J. Am. Chem. Soc., 1991, 113, 1046.

10. Sharp, K.G.; Sutor, P.A., Williams, E.A.; Cargioli, J.D.; Farrar, T.C.; and Ishibitsu, K. J. Am. Chem. Soc.,1976, 98,1977.

11. Cypryk, M.; Fossum, E.; Matyjaszewski, K. in preparation

12. Henning, J.C.M. J. Chem. Phys., 1966, 44(5), 2139.

13. Makarov, I.G.; Kazakova, V.M.; Syrkin, Y. J. Organomet. Chem., 1969, 8, 231.

14. Cadberry, E.; West, R.; Glass, G. E. J. Am. Chem. Soc., 1969, 19, 5446.

15. Brough, L. F. and West, R. J. Organomet. Chem., 1980, 194, 139.

16. Gerson, F.; Heinzer, J.; Bock, H.; Alt, H.; Seidl, H. Helvetica Chimica. Acta, 1968, (51) 4, 707.

17. Sipe, H. J. and West, R. J. Organomet. Chem., 1974, 70, 353.

18. Kumada, M. and Ishikawa, M. J. Organomet. Chem., 1963,1, 153.

19. Ruehl, K. E. and Matyjaszewski, K. J. Organomet. Chem., 1991, 410, 1.

20. Kumada, M.; Ishikawa, M.; and Maeda,S. J. Organomet. Chem.,1964, 2, 478.

21. Sakurai, H.; Tominaga, K.; Watanabe, T.; and Kumada, M. Tetrahedron Letters, 1966, 45, 5493.

22. Laguerre, M.; Dunogues, J.; Calas, R. J. Chem. Soc. Chem. Comm., 1978, 272.

Scheme 1:

$$Ph(SiMe_2)_2Cl + 2\ Li \xrightarrow{-\ LiCl} Ph(SiMe_2)_x^- {}^+Li \rightleftharpoons 1/6(SiMe_2)_6 + PhSiMe$$

Scheme 2:

$$PhSiMe_2^- {}^+Li + 1/6(SiMe_2)_6 \overset{Keq}{\rightleftharpoons} PhSiMe_2SiMe_2{}^- {}^+Li$$

Scheme 3:

Stage 1:

$$Ph(SiMe_2)_2Cl + 2\ Li \longrightarrow Ph(SiMe_2)_2^- {}^+Li + LiCl$$

Cl-2 *A- 2*

$$Ph(SiMe_2)_2Cl + Ph(SiMe_2)_2^- {}^+Li \longrightarrow Ph(SiMe_2)_4Ph + LiCl$$

Cl-2 *A-2* *L-4*

Stage 2:

$$Ph(SiMe_2)_4Ph + Li \longrightarrow [Ph(SiMe_2)_4Ph]^- {}^+Li$$

L-4 *RA-4*

$$[Ph(SiMe_2)_4Ph]^- {}^+Li \longrightarrow Ph(SiMe_2)^-{}_n{}^+Li + Ph(SiMe_2)_{4-n}$$

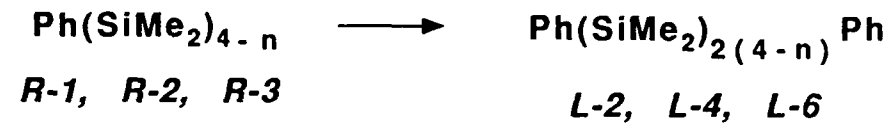
RA-4 *A-1, A-2, A-3* *R-1, R-2, R-3*

$$Ph(SiMe_2)^-{}_n{}^+Li + Ph(SiMe_2)_2Cl \longrightarrow Ph(SiMe_2)nSiMe_2SiMe_2Ph$$

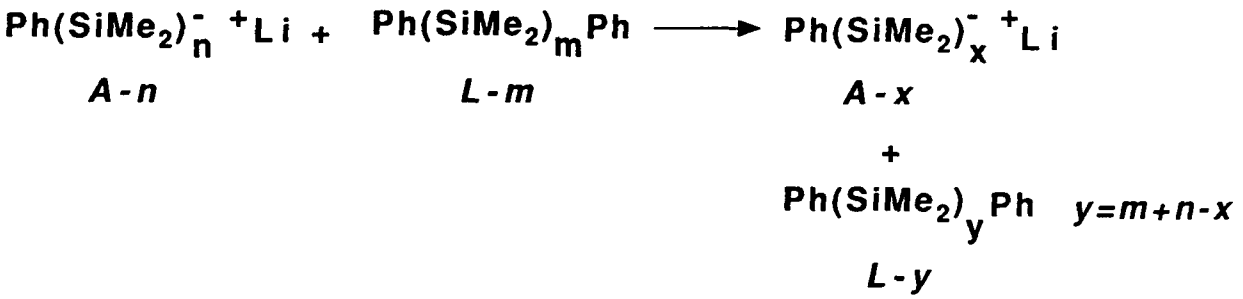
A-1, A-2, A-3 *Cl-2* *L-3, L-4, L-5*

$$Ph(SiMe_2)_{4-n} + Li \longrightarrow Ph(SiMe_2)^-_{4-n}{}^+Li$$

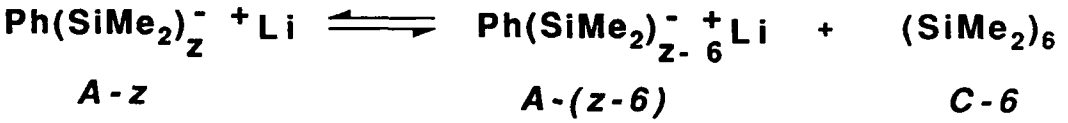
R-1, R-2, R-3 *A-1, A-2, A-3*



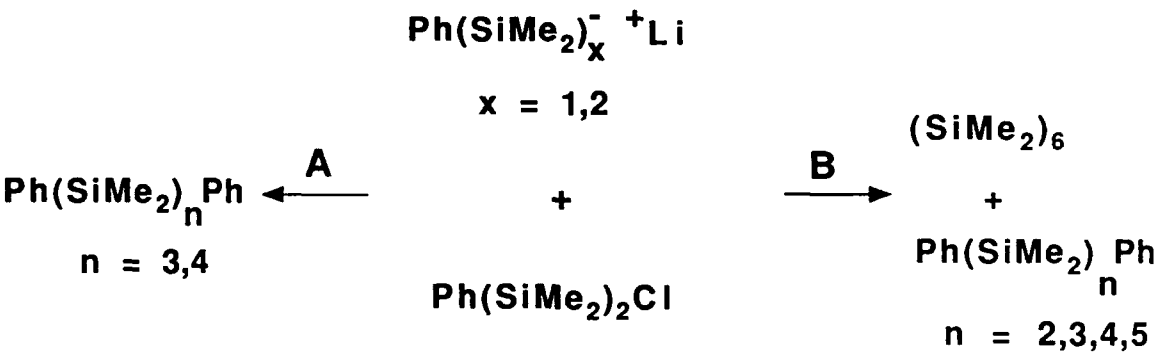
Stage 3:



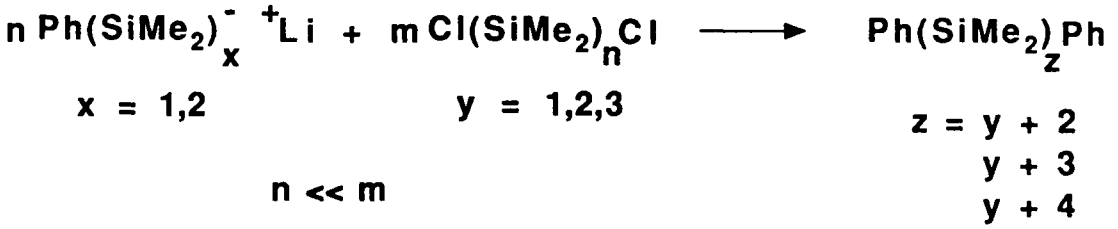
Stage 4:



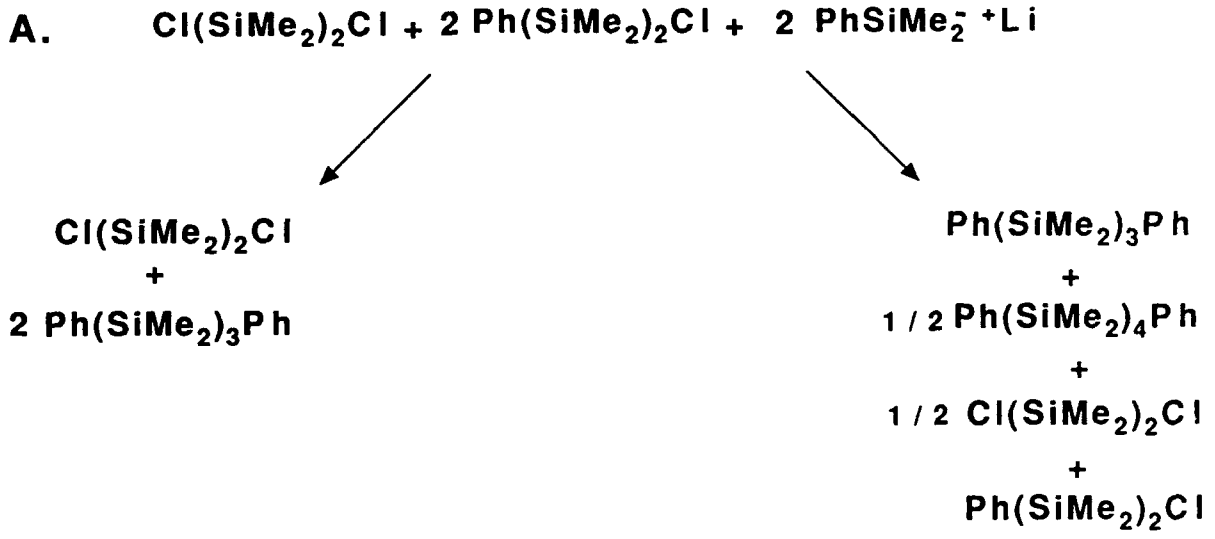
Equation 1:



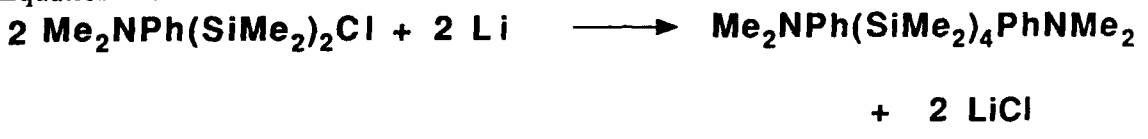
Equation 2:



Equation 3:



Equation 4:



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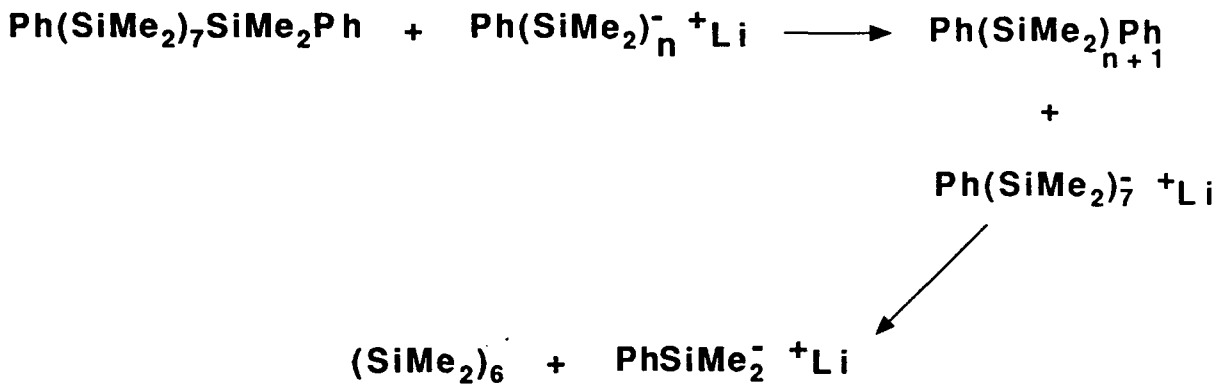

Table 1:

	$PhMe_2SiMe_2SiCl$	$PhMe_2SiMe_2Si{:}Li^+$	shift (from Cl to Li)
ipso	137.4	149.0	downfield 11.6 ppm
ortho	134.9	134.4	approx. same
meta	128.8	128.6	approx. same
para	130.0	127.1	upfield 2.9 ppm
methyl	2.5, -4.2	1.45, -1.92	upfield > 1ppm

Table 2:

	$PhMe_2SiCl$	$PhMe_2Si{:}Li^+$	shift (from Cl to Li)
ipso	137.0	166.0	downfield 29 ppm
ortho	133.8	133.8	approx. same
meta	128.8	126.5	approx. same
para	131.0	122.7	upfield 8.7 ppm
methyl	2.3	7.5	downfield 5 ppm